RESOLUTION CONSULTANTS

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Subject: Review of Draft CSIA Results — NWIRP Bethpage

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Draft CSIA Results Review

This technical memorandum provides a review of the Compound Specific Isotope Analysis (CSIA) sampling report provided by Henningson, Durham & Richardson Architecture and Engineering, P.C. (HDR). HDR provided brief "notes" to accompany the draft CSIA Forensic Report submitted by Pace Analytical (Pace). The Pace report is dated 6 April 2016, and the HDR notes are dated 12 April 2016.

It is the Navy's understanding that the use of the CSIA sampling is to identify discrete sources to groundwater contamination by use of their isotopic signature. Based on the sampling locations, it is also apparent that the sampling was predisposed to identify an upgradient well on former Northrop Grumman property within operable unit (OU) 3, and an apparent upgradient plume within OU2. The Pace report provides a summary of the site history and sampling plan, including a site figure of the monitoring well network and the selected wells sampled for this investigation. Pace goes on to provide a detailed discussion of sample preparation, CSIA analytical methodology, limitations, and data processing/interpretation. General concepts of isotopic fractionation/enrichment and isotopic variability amongst sources are also presented. HDR's memorandum is extremely brief, summarizing results of the TCE and 1,4-Dioxane (1,4-D) analyses, but provides no additional insight. The Pace document would have served as a sufficient stand-alone documentation of the results, and was used as the

primary basis of this review. This review presents a) a listing of the inherent limitations; b) specific critique of conclusions made in the HDR and Pace reports; and c) review conclusions.

Limitations:

There exists a number of severe limitations with this sampling effort. Among the limitations are several obvious issues noted prior to the instigation of the CSIA investigation, namely:

- **Detection limits** – The CSIA technique requires sufficient concentrations of analyte in the sample to allow for the detection of isotopes such as ^{2}H (deuterium), which has a natural abundance of less than 0.02% of all hydrogen isotopes. It is not surprising that the majority of the deuterium results for the 1,4-D analyses were below the analytical detection limit, eliminating their use for source isotopic identification.
- **Impact of degradation reactions** – The age of the plume allows for sufficient time for biodegradation to occur to some degree. Subsequently, the ability to identify a "pure" source area (e.g., a well that is upgradient in a known source area, and therefore expected to be isotopically distinct from other "source" areas, and unaffected by geochemical reactions or flow perturbations induced by anthropogenic stresses to the aquifer) can be limited. Pace notes that the upgradient sample (BCP MW-4-1, as interpreted by Pace) is more degraded than those mid-plume, and that the leading edge has also significantly degraded. This aging and consequent biodegradation effect complicates the ability to effectively resolve multiple sources, should they exist.
- **Likelihood of a common TCE vendor** – Most significantly, the Navy anticipated that the ability of CSIA to resolve multiple sources would be rendered ineffective due to the likelihood that any TCE-user in the area would purchase TCE from a common vendor. Solvent vendors are not historically common, and the fire-hazard associated with shipping solvents make sourcing TCE from remote vendors unlikely. It is, therefore, most plausible that any TCE used in the area was sourced from the same regional vendor. If all potential sources purchased solvents from the same vendor, any resulting solvent plumes would have the same isotopic signature.
- **Process variability** – Any variation within the solvent manufacturing process, such as minor process modifications or changes in the ingredient sourcing, would result in significant variability in the pure TCE isotopic signature over time. Because historical process quality control on manufacturing batches was not comparable to modern methods, the isotopic signature of any single distributor over time cannot be resolved with any reasonable degree of scientific certainty.
- **Limited sample collection** – The ability of this sampling program to identify and resolve multiple sources of CSIA was extremely limited due to the design of the sampling program. For example, there is no apparent attempt to match the wells to each other within the hydrogeologic sequences in the Magothy, and the sampling is predisposed to utilize upgradient wells within OU2 and OU3 (GM-73D2 and BCP MW-4-1, respectively). Both HDR and Pace noted that the scope of the current sampling program was extremely limited and intended to serve as a "proof of concept". Because the program could not

and did not identify any "pure" source areas from which a parent population could be derived, any samples that show evidence of potential co-mingling cannot be further interpreted. Unless pure source areas can be identified (which is unlikely given the aforementioned issues), there is no possible way to apply standard isotopic population statistics, such as the IsoError stable isotope mixing model developed by Phillips and Gregg (2001). Given the limitations and issues related to the mixed data interpretation, the only concept that this work successfully proved was that CSIA is ultimately ineffective for this particular site.

Specific Critique of CSIA Report Conclusions:

Excerpt from HDR memorandum:
"In summary, Pace has concluded that the TCE results are inconclusive, in that there are insufficient data to determine whether the TCE is emanating from one or more distinct sources. The 1,4-D CSIA results indicate two distinct sources are present and that these commingle in downgradient wells."

Critique:
The Navy agrees with the inconclusiveness of the TCE data. For the 1,4-D data, there is no rationale presented as to how the CSIA results show two distinct sources, nor are they identified. The statement of comingling is clearly conjectural, and cannot be substantiated to any reasonable degree with this data.

From Pace Forensics Report:

Table 1 Concentrations of 1,4-D and select VOC contaminants in samples from the GABF site

Pace CSIA	Client	Concentrations of Contaminants (µg/L)							
Lab ID	Sample ID	1,4-D	VC	cDCE	TCE	PCE	11DCA	111TCA	Freon-113
18242-2	BCP MW-4-1	116	390	390	99	1.5	18	4.6	<1
18233-2	GM73D2	7.6	<1	<1	33	1.4	<1	<1	<1
18242-1	RE122D1	12.9	<1	1.8	590	1.5	<1	<1	4.3
18233-1	TT101D2	4.1	<1	2.0	590	<1	<1	<1	19
18232-2	BPOW3-4	3	<1	<1	73	<1	<1	<1	<1
18232-1	BPOW3-2	6	<1	<1	<1	<1	<1	<1	<1

As seen in **Table 1**, contaminants were detected in the highest concentrations at locations between the presumed upgradient well, BCP MW-4-1 and the presumed downgradient well, TT101D2. TCE in well BCP MW-4-1 (99

Critique:

This statement is entirely incorrect with respect to contaminant distribution – the highest concentrations of 1,4-D (by an order of magnitude) is in the presumed upgradient well far to the NE (BCP MW-4-1); the general groundwater flow direction (SSE) does not place the other five wells downgradient of BCP MW-4-1. For TCE, the highest concentrations are actually in the mid-plume wells, potentially indicating an upgradient source to the NW (upgradient) of the impacted wells, consistent with a SSE flow direction.

From Pace Report, Page 15:

It can't be ruled out that there is more than one source and that the limited sample set and the extensive degradation in BCP-MW-4-1 and BPOW3-4 have made it such that this study can't identify the additional sources. Further, the possibility must be considered that these facilities shared a common TCE vendor. There is a possibility since these facilities operated at the similar time and were geographically very close. If they each had TCE from the same source, there would be no isotopic differences.

Critique:

Agree, as provided in the known limitations listed above.

From Pace Report, Page 16:

Based on the findings of this initial study, it appears that the TCE plume had a single source; however, that could not be absolutely determined because of a number of confounding issues (e.g., potential effect of biodegradation). It also appeared that there were two separate 1,4-D sources that co-mingled in the downgradient wells, but again that could not be unambiguously proven.

Critique:

The conclusion of two separate sources of 1,4-D comingled downgradient is not justified further than this statement in the Pace report. For example, no analysis/explanation of the degree of carbon fractionation difference is provided – how is less than an order of magnitude judged to be sufficient to label samples as being sourced separately? Furthermore, the "sources" were not identified, nor was the evidence for "comingling" – these statements are purely conjectural and are scientifically objectionable without clear supporting data coupled with explanation.

As for "proof of concept", CSIA has been used successfully at other sites. At this site, however, several factors will eliminate the possibility of this type of analysis being successful in defining separate sources:

- There are multiple isotopic signatures from multiple quality batches, all likely purchased from the same vendor;
- There are multiple stresses on the aquifer from high volume production wells and remediation wells; this makes it even more difficult to define "upgradient";
- The concentrations of 1,4-D are too low to provide meaningful results with respect to deuterium;
- The sensitivity of the results to biodegradation precludes definitive isotopic differentiation for TCE.

In conclusion, the CSIA sampling was designed and initiated with an apparent disregard to the inherent limitations of the study. The sampling report provides no results that can be used to arrive at any conclusions regarding the chemical distinction of sources in the area with any reasonable degree of scientific certainty, and in fact the site specific limitations discussed in the body of this memorandum render any such conclusions impossible.